AGRICULTURAL PRODUCT-DERIVED CARBON FOR ENERGY, SENSING, AND ENVIRONMENTAL APPLICATIONS: A MINI-REVIEW

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Abstract

Carbon is one of the versatile materials used in modern life for human welfare. It has a wide range of applications such as drug delivery, coatings, energy generation and storage, gas separation, water purification, sensor fabrication, and catalysis. Most of the widely used carbon materials are graphene and carbon nanotubes. Nonrenewable precursors (e.g., natural gas), toxic chemicals, and complex synthesis methods are often required for their preparation, limiting their wide practical applications. Besides these, biomass-derived carbons are attractive materials as they can be prepared simply from renewable biomass. However, their practical applications' success partially depends on their properties like size, shape, porosity, and presence of heteroatoms, which can be controlled by selecting the proper type of biomass, activating agent, and preparation method. It is noted that different species of plants have different chemical compositions and textures. This mini-review summarizes our group's recent sophisticated developments in agricultural-bio-waste-derived carbonaceous materials, including nanomaterials for electrocatalytic water splitting, electrochemical sensors, supercapacitors, water splitting, water treatment, gas separation, and enhance oil recovery. This offers valuable insights and essential guidelines towards the future design of agro-waste derived carbonaceous materials in various applications.

Graphical Abstract

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Introduction

Carbon is one of the versatile materials used in modern life for human welfare. It has a wide range of applications such as drug delivery, coatings, energy generation and storage, gas separation, water purification, sensor fabrication, and catalysis. Most of the widely used carbon materials are graphene (Li et al., 2009) and carbon nanotubes (Aziz and Yang 2008, 2007; Aziz et al., 2007). Nonrenewable precursors (e.g., natural gas), toxic chemicals, and complex preparation methods are often required for their preparation, limiting their wide practical applications. Besides these, agro-waste-derived carbonaceous materials (ADCs) are universal, essential, and attracting much interest for their unique architecture and widespread applications. It is noted that a huge amount of agro-waste, which is more or less responsible for environmental pollution, is generated all over the world, particularly in tropical countries like Bangladesh, India, Pakistan, and Malaysia. This indicates that the preparation of valuable and useful ADCs is important. ADCs are extensively used in different fields, including sensing (Aziz et al., 2020; Ahammad et al., 2019a; Ahammad et al., 2019b; Ahammad et al., 2018; Haque et al., 2020a; Aziz et al., 2017; Haque et al., 2020b), microbial fuel cells (Senthilkumar et al., 2020), filtration/separation (Aziz et al., 2019; Khan et al., 2020), oil recovery (Haq et al., 2019), electrochemical water splitting (Shah et al., 2019; Buliyaminu et al., 2020), electrode materials for supercapacitors (Mohamedkhair et al., 2020; Islam et al., 2020; Shah et al., 2020; Deb Nath et al., 2019; Aziz et al., 2020), and in other emerging technology applications. In addition, unique properties of the ADCs like versatile porosity, high specific-surface-area (SSA), and high electrical and thermal conductivities attracted much attention of the researchers to utilize them in various applications. So far, our group has used a variety of agricultural by-products of different species such as jute (Corchorus spp.) sticks and fibers (Aziz et al., 2020; Aziz et al., 2019; Ahammad et al., 2019b), tal palm (Borassus flabellifer) leaves (Ahammad et al., 2019a), taro (Colocasia spp.) stems (Ahammad et al., 2018), rice (Oryza sativa) husk (Haque et al., 2020b), date palm (Phoenix dactylifera) leaves (Haq et al., 2020; Aziz et al., 2017), bhat (Clerodendrum infortunatum L.) leaves (Haque, et al., 2020a), rain tree/monkeypod tree (Samanea saman) leaves (Khan et al., 2020), siris (Albizia procera) leaves (Buliyaminu et al., 2020; Shah et al., 2019; Mohamedkhair et al., 2020), algae (Pithophora polymorpha) filaments (Shah et al., 2020), banana (Musa sapientum L spp. sylvestris) leaves (Roy et al., 2020), and jam (Syzygium cumini) leaves (Deb Nath et al., 2019) as appropriate precursors for the preparation of efficient and low-cost ADCs. It is to mention that these plants are produced in most parts of the world, including Bangladesh. The selection of proper agro-waste plays an important role in ADC properties as the different species have different chemical compositions and textures.

The efficient use of ADCs relies not only on their impressive physical and chemical properties, such as electrical and thermal conductivities, stability, high SSA, and low density, but also on their wide availability. In the last few decades, extensive progress has been made in carbon synthesis, both through advancements in the existing protocols and practical designing of new synthetic methods. Some of the conventional protocols for the synthesis of activated carbons (ACs) and simple carbons are chemical and physical activation (Aziz et al., 2020; Ioannidou and Zabaniotou 2007) and simple carbonization of agricultural by-products at high temperatures (Aziz et al., 2020; Lohri et al., 2016), respectively. In the chemical activation process, the precursor materials are mixed with activating agents, for example, KOH, NaHCO₃, ZnCl₂, H₃PO₄, and K₂CO₃ and pyrolyzed at different temperatures under an inert atmosphere. In contrast, physical activation involves the precursor materials' carbonization under an inert environment, followed by the resulting char's activation at high temperature (700 to 1100°C) under carbon dioxide or water vapors atmosphere. As chemical activation involves a single step coupling carbonization with activation at low temperature, therefore chemical activation is preferable to physical activation. It
also results in ACs production with a well-developed porous structure, low-cost, and high yields. The production of efficient ACs depends upon the preparation conditions. The balancing of the preparation requirements is challenging for researchers, as many resultant characteristics and operating variables need to be taken into consideration. The conditions for the preparation of ACs must be balanced appropriately to acquire ACs with desirable properties. The major factors of the preparation methods which affect the properties of ACs from biomass are the selection of suitable biomass, chemicals, activation temperature, and activation time (Aziz et al., 2020).

Broad pore-size distribution, including both micro- and meso-porous regions, has been identified for the ACs predominantly used in adsorption, separation, catalysis, and electrode materials. ACs are not pure elemental carbon but contain different atoms like hydrogen, oxygen, nitrogen, and sulfur as significant constituents in varying proportions, depending upon the raw materials’ nature. Some of these atoms enter the structure of ACs during preparation and activation processes. The presence of heteroatoms on the surface determines the surface chemistry and the ACs application capacity. Hydrogen/oxygen is present as a residual element, distributed throughout the carbon surface, while oxygen is also introduced due to the carbon's oxidation during preparation and activation. The oxygen and hydrogen combine with the carbon surface and result in different surface functional groups. The major surface functional groups on the ACs are hydroxyl groups (–OH), carbonyl groups (>C=O), carboxylic groups (–COOH), aromatic groups, lactone groups, and hydrolytic ether structures. ACs also contains small ash content in the form of oxides and salts of Si, Fe, Mg, Ca, Zn, Pb, Al, and Na and pure metals. The presence of ash causes defects in the elementary structure of the ACs. Oxygen is chemisorbed at the defects, which lead to increased adsorption of polar substances. Moreover, the ash contents soluble in aqueous solutions affect the adsorption of adsorbate by co-adsorption along with adsorbate, thus changing the adsorptive characteristics of the ACs.

The conversion of agro-wastes into precious carbonaceous materials can also solve environmental problems such as increased agricultural waste, causing atmosphere and water contamination through the natural degradation process (Danish and Ahmad 2018; Ashraf et al., 2020). The availability and utilization of agro-wastes to produce low-cost and efficient ADCs materials have proven to be potentially raw materials for the synthesis of ACs. The ACs have proved to be ideal materials for diverse applications, including sensors, energy storage, and water treatment. But its widespread usage is limited, due to the expense of production, which has triggered the researchers on the feasible alternative for the cost-effective production of carbon materials from biomass (Danish and Ahmad 2018). The implementation of biowaste has been extensively investigated as a possible alternative to costly methods of carbon production. A comprehensive list of ADCs prepared by our group from various agricultural byproducts and their diverse applications are presented thoroughly in this mini-review.

Preparation of ADCs

The preparation of carbon materials, including nanomaterials from economic, renewable, and abundantly available agricultural resources utilizing environmentally friendly techniques, is a promising research area in science and technology. Due to the abundant availability and low-cost of agricultural waste and the unique physical, chemical, and electrochemical properties of the ADCs, they are widely used in a variety of applications. ADCs have been prepared by various methods in laboratories by using multiple activating agents and different preparation conditions. Recently, Aziz et al. (2020) have reported a fascinating study on the preparation and applications of jute-derived carbon. This report reviewed broad research in the field of ADCs preparation from the renewable, environmentally friendly, widely available, and low-cost jute fibers and sticks. Several necessary preparation protocols in designing ADCs materials were discussed in more
detail, involving simple pyrolysis, physical activation, and chemical activation. The procedures for ADCs preparation from jute fibers and sticks are schematically represented in Fig. 1.

Aziz et al. (2019) also prepared highly porous carboxylated ADCs from jute sticks. The jute sticks were cut into small pieces, washed, dried, and pulverized. NaHCO$_3$ was mixed with the jute powder (4:1 w/w.), which acts as an activating agent. The mixture was heated at 850 °C in a tube furnace under a N$_2$ atmosphere for 5 h with a 5 °C/min heating and 10 °C/min cooling rates. The carbonized product was washed and dried at 60 °C to get ADCs. The schematic procedure for the jute derived ADC preparation is shown in Fig. 2. The ADCs were further functionalized with concentrated HNO$_3$ and H$_2$SO$_4$ (1:3 v/v.) and ultrasonication. The prepared ADCs exhibited a combined micro-, meso-, and macro- porous structure with a high SSA of 615 m$^2$/g.

Ahammad et al. (2019b) prepared activated jute carbon paste by chemical activation of jute sticks at 850 °C, using ZnCl$_2$ as an activating agent. Initially, the clean, dried, and 100 µm sieved
powder of jute sticks were mixed ZnCl₂ (1:1 w/w.) and pyrolyzed at 850 °C in a tube furnace for 5 h under the N₂ atmosphere. Secondly, the carbonized product was washed with 0.5 M HCl and de-ionized (DI) water and dried at 60°C for 12 h to remove the impurities. The resultant ADCs from jute sticks exhibited a high SSA of ~1450 m²/g with a 3.6 nm average pore diameter. Fig. 3 presents the field emission scanning electron microscopy (FESEM) images of the jute-derived ADCs, representing a highly smooth surface area.

Shah et al. (2019) prepared ADCs by simple pyrolysis of Albizia procera leaves at 800°C under a N₂ environment. The Albizia procera leaves were washed, dried, and pulverized to prepare fine powder with particle size less than or equal to 100 µm. The prepared powder was heat-treated in a tube furnace at 800°C for 5 h with heating and cooling rates of 10°C/min and 5°C/min, respectively. The carbonized powder was washed with 0.1 M HCl and DI water to eliminate any impurities. Similarly, Mohamedkhair et al. (2020) reported the effect of activating agents on the preparation of ADCs from Albizia procera leaves. NaHCO₃ and ZnCl₂ activating agents were used in the preparation of ADCs, and their impact on surface functional groups, textural and structural properties, and SSA were compared. The ADCs prepared with NaHCO₃ as an activating agent exhibited the highest SSA of 910 m²/g. Aziz et al. (2017) reported the ADCs preparation from date palm leaflets by simple pyrolysis in a N₂ atmosphere. Date leaves were washed with DI water.
multiple times and dried at 70°C in an electric oven for 24 h. The leaflets from the date leaves were separated and sliced into 2 cm long pieces. The cut pieces were then put in a flat alumina crucible and placed in a high-temperature tube furnace. Afterward, N₂ gas was purged into the tube of the furnace, and the product was pyrolyzed at 850°C for 5 h with heating and cooling rates of 10°C/min and 5°C/min, respectively. The detailed procedure for the preparation of ADC from date palm leaflets is described in Fig. 4. In another study Haq et al. (2019) prepared ADCs from date leaves using simple pyrolysis, and then carboxylic acid functionalization was carried out to make the product water-soluble. The powder of date leaves was mixed with KHCO₃ (1:4 w/w.) and heated at 850°C for 5 h under a N₂ atmosphere with a 10 °C/min heating rate and 5°C/min cooling rate. The carbonized product was washed with 0.5 M HCl and DI water and finally dried at 60°C for 24 h to obtain the porous ADCs nanosheets. Similarly, various agricultural wastes have been used for the preparation of efficient ADCs materials, including tal palm leaves (Ahammad et al., 2019a), jam leaves (Deb Nath et al., 2019), bhat leaves (Haque et al., 2020a), rain/monkey pod tree leaves (Khan et al., 2020), rice husks (Haque 2020b), taro stems (Ahammad et al., 2018), *Pithophora polymorpha* filaments (Shah et al., 2020), banana leaves (Roy et al., 2020), and waste tissue paper scraps (Senthilkumar et al., 2020).

![Fig. 4. Schematic representation for the preparation of nanostructured ADC electrode from date palm leaflets. Reproduced with permission (Aziz et al., 2017). Copyright 2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.](image)

**Applications of ADC**

ADCs are recognized as the most promising materials, thanks to their favorable chemical and physical properties, including low-cost, chemical-stability, tunable-microstructure, and surface functional groups. Appropriate utilization of ADCs materials could grab a variety of applications. The realization of useful materials has been a vital objective to accomplish more efficient and environmentally friendly purification and separation processes (Li et al., 2016; Usman et al., 2020). In a recently published review by Aziz et al. (2020) have reported various potential applications of the jute sticks and fibers derived ADCs in the field of sensors, water treatment, and energy storage. They also emphasized various future potentials of ADCs prepared from jute sticks and fibers, including their utilization in electrochemical/electrical/electronic industries, coatings, solar cells, drug delivery, fuel cells, oil enhancement recovery, pharmaceuticals, catalysts, and steel preparation. The preparation of jute derived ADCs, and their various applications are summarized in Fig. 5.
Aziz et al. (2019) and Chowdhury et al. (2020) prepared carboxylated ADCs from jute sticks and used it for the removal of Pb\(^{2+}\) from aqueous solution under different experimental conditions such as pH, temperature, contact time, and initial concentration. The prepared ADCs were tested for 25 and 10 mg/l of Pb\(^{2+}\) at different temperatures (27 and 15°C), pH (7.0 and 4.0), and contact periods (1 to 60 min). Within 15 min of contact time, ~99% of Pb\(^{2+}\) was achieved from the tested sample. The carboxylated ADCs from jute sticks may be used for quick and easy removal of toxic elements from aqueous solutions and exhibit a strong potential for household and industrial applications.

Aziz et al. (2017) reported a simple substrate-free electrode comprising ADCs from date palm leaflets for direct use as an economical electrode material. The prepared ADC was used as an electrocatalyst for the sensitive detection of hydroquinone and demonstrated a limit of detection of ~6 µM. The prepared electrodes were highly stable and selective for the determination of
hydroquinone. Ahammad et al. (2019b) constructed an electrochemical nitrite sensor using a screen-printed fluorine-doped tin oxide electrode with ADCs from jute sticks. The prepared sensor was used for amperometric detection of nitrite, and a limit of detection of 437 nM and sensitivity of 863.71 μAmM⁻¹cm⁻² was obtained toward nitrite. The sensor was very stable and can be used in the existence of various interferences. The experimental results suggested that jute-sticks could be used in the fabrication of low-cost and efficient environmental contaminant sensors. Fig. 6 presents the influence of jute sticks derived ADC on the sensitive detection of nitrite. In another study, Ahammad et al. (2019a) fabricated an electrochemical sensor for the simultaneous determination of uric acid and dopamine using porous tal palm derived ADCs nanosheets. The sensor delivered a limit of detection of 0.078 μM and 0.17 μM and sensitivity of 2.693 μAmM⁻¹cm⁻² and 1.2057 μAmM⁻¹cm⁻² for dopamine and uric acid, respectively.

Similarly, Ahammad et al. (2018) reported an electrochemical sensor based on gold nanoparticles coated ADCs derived from taro stems from selective dopamine detection. The prepared sensor demonstrated a linear response in the dopamine concentration range from 0.5 μM to 250 μM with a limit of detection of 0.25 μM. Similarly, Haque et al. (2020b) reported hollow reticular-shaped ADCs derived from rice husks for uric acid and dopamine simultaneous detection. The possible oxidation mechanism for the analytes was discussed in detail, and the sensor was tested for stability, reproducibility, and interference. In another study, Haque et al. (2020a) prepared nitrogen-doped ADCs from bhant leaves and applied as an electrocatalyst for ketoconazole detection. The prepared ADCs based electrochemical sensor’s performance was tested in phosphate buffer solution (pH 3.0), and a limit of detection of 3 μM with a linear concentration range from 47 μM to 752 μM was achieved. The results confirmed the potential of ADCs as an electrocatalyst for the detection of ketoconazole. Khan et al. (2020) reported the preparation of carboxylated ADCs nanosheets from rain/monkeypod tree leaves, blended with polyetherimide membranes, for improved CO₂/CH₄ separation. The schematic representation for the preparation of carboxylated ADCs nanosheets from rain/monkeypod tree leaves and their application in separation of CO₂/CH₄ is shown in Fig. 7A, and the corresponding FESEM image of the obtained ADC is shown in Fig. 7B.

![Fig. 7.](image-url)
Electrode materials are the most critical component of electrochemical energy storage devices (e.g., supercapacitors), at which the overall charge storage capacity depends (Islam et al., 2020). Mohamedkhair et al. (2020) applied the prepared naturally nitrogen-doped ADCs from Albizia procera leaves as electrode materials for supercapacitors. The ADCs prepared with NaHCO₃ as an activating agent delivered the highest specific capacitance of 231 F/g at a current density of 1 A/g in 1 M H₂SO₄ aqueous electrolyte. Deb Nath et al. (2019) prepared defective ADCs from Syzygium cumini leaves for supercapacitor electrodes. The prepared ADCs exhibited structural defects of 0.72, a high SSA of 1184 m²/g, electrical conductivity of 0.0123 S/cm, and contained sufficient oxygen-containing functional groups. These properties of the ADCs lead to deliver a high specific capacitance of 222 F/g when used as electrode materials. Shah et al. (2020) reported the composite of heteroatoms enriched carbon derived from Pithophora polymorpha and polyaniline as electrode materials for high performance supercapacitors. The hierarchical porous ADC was prepared by direct pyrolysis of the Pithophora polymorpha filaments, and polyaniline was successfully deposited via electrochemical deposition on the prepared ADC. The resultant composite was used as electrodes for supercapacitors, which exhibited pseudocapacitor behavior and yielded a high areal capacitance of 176 mF/cm² at a scan rate of 1 mA/cm² with a high specific energy and specific power of 24.5 μWh/cm² and 500 μW/cm², respectively. Recently Roy et al. (2020) have reported hierarchical porous ADCs for supercapacitor applications. The ADCs were prepared by simple activation of banana leaves with K₂CO₃, which produced highly efficient ADCs with a high specific surface area of ~1459 m²/g. The electrochemical energy storage performance of the reported ADC was investigated using symmetric supercapacitors. The fabricated supercapacitors were tested in various electrolytes, which yielded the specific capacitances of 190, 114, and 55 F/g in pure ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]), organic 1 M tetraethylammonium tetrafluoroborate in acetonitrile, and aqueous 0.5 M sodium sulfate electrolytes, respectively. The ADCs also showed a wider operating potential window, highest energy density, and high-power density of 3V, 59 Wh/kg, and 750 W/kg in the [BMIM][PF₆], respectively. The environmentally friendly, low cost, and electroactive ADCs materials could play an important role in the applications of energy storage devices such as supercapacitors and batteries.

Fig. 8. (a) Schematic representation for Albizia procera derived ADC and manganese oxide nanocomposite, and (b) their corresponding application as electrode material in electrochemical water oxidation. Reproduced with permission (Shah et al., 2019). Copyright 2019, Springer Nature.
Shah et al. (2019) prepared manganese oxide nanoparticles-coated Albizia procera derived carbon (MnO\textsubscript{x}-ADCs) by direct thermal decomposition for electrochemical water oxidation. Various compositions of MnO\textsubscript{x}-ADCs were prepared by keeping the constant concentration of ADCs (200 mg) and changing the MnO\textsubscript{x} precursor concentrations (500 to 1500 mg). Considerable differences in the electrochemical properties of the prepared samples were observed towards water oxidation. The results demonstrated that the compositions of MnO\textsubscript{x}-ADCs played a significant role in being used as catalysts for electrochemical water oxidation. The schematic representation for Albizia procera derived ADC and manganese oxide nanocomposite and their corresponding application as electrode material in electrochemical water oxidation is shown in Fig. 8. Similarly, Buliyaminu et al. (2020) reported the preparation of cobalt oxide nanoparticles and Albizia procera derived ADCs (Co\textsubscript{3}O\textsubscript{4}-ADCs) by direct thermal decomposition and their application as a catalyst for electrochemical water oxidation. The prepared samples were immobilized on the filter paper derived carbon electrode and studied their electrocatalytic properties toward water oxidation and produced a current density of 28 mA/cm\textsuperscript{2} at 1.5 V with electrochemical water oxidation starting potential of 0.7 V.

Furthermore, ADCs are significantly important electrode materials due to their unique structural and electrochemical properties, demonstrating improved performance and robust stability in various environments (Senthilkumar et al., 2020). Thus, the freestanding electrodes with fascinating characteristics simplify the electrode fabrication and reduce the overall cost of electrodes that encourages the cost-effective strategy for green energy generation and storage. Haq et al. (2019) reported ADCs prepared from date leaves for enhancing oil recovery. ASTM D 971-99a method was used to measure the interfacial tension between crude oil and the prepared ADCs and obtained the critical micelle concentration and perform a core flood experiment. A critical micelle concentration was found at 600 ppm, with an interfacial tension of 8.56 dyne/cm.

**Conclusions**

Here we have summarized our group’s recent developments in ADC materials for electrocatalytic water splitting, electrochemical sensors, supercapacitors, water splitting, water treatment, gas separation, and enhance oil recovery. The precursors of carbonaceous nanomaterials are low-cost and available agricultural-biowastes, which could replace commercially available resources. Activation/pyrolysis of agricultural-biowastes is a practical approach to utilize the garbage and wastages into an environmentally friendly procedure to prepare the active carbonaceous materials, including nanomaterials. It has been recognized that porous carbonaceous materials, including nanomaterials with rich porosity, high SSA, and modified surface chemistry, are crucial for further boosting electrochemical applications. To date, numerous carbonaceous nanomaterials, including ADCs, have been used extensively in the fabrication of electrochemical sensors, electrocatalysts, and electrode materials for supercapacitors and batteries. The naturally abundant agricultural-biomass resources with intriguing physical and chemical structures are distinctive with the ability to open unique possibilities for developing innovative carbonaceous materials for sensors, high-performance supercapacitors, efficient electrocatalysts, oil enhance recovery. Moreover, ADCs exhibits an extensive potential to be used in a broad range of applications, including fuel cells, electrochemical/electrical/electronics, catalysts, solar cells, steel preparation, oil enhancement recovery, pharmaceuticals, drug delivery, coatings, energy storage, and production of more valuable carbon like graphene and nano-graphite.
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